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## INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

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<b>(21) International Application Number:</b> PCT/EP99/00003 <b>(22) International Filing Date:</b> 4 January 1999 (04.01.99) <b>(30) Priority Data:</b> MI98A000021 9 January 1998 (09.01.98) IT <b>(71) Applicant (for all designated States except US):</b> LONZA S.P.A. [IT/IT]; Via Vittor Pisani, 31, I-20124 Mailand (IT). <b>(72) Inventors; and</b> <b>(75) Inventors/Applicants (for US only):</b> CASTIGLIONI, Gian, Luca [IT/IT]; Via Roseto, 15, I-47036 Riccione (IT). FUMAGALLI, Carlo [IT/IT]; Via C. Albani, 2/a, I-24061 Albano S. Alessandro (IT). <b>(74) Agents:</b> RAUBER, Beat et al.; Lonza AG, Patentabteilung, Postfach, CH-4002 Basel (CH).		<b>(81) Designated States:</b> AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, CA, CH, CN, CU, CZ, DE, DK, EE, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MD, MG, MK, MN, MW, MX, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TR, TT, UA, UG, US, UZ, VN, YU, ZW, ARIPO patent (GH, GM, KE, LS, MW, SD, SZ, UG, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GW, ML, MR, NE, SN, TD, TG).  <b>Published</b> <i>With international search report. Before the expiration of the time limit for amending the claims and to be republished in the event of the receipt of amendments.</i>
<b>(54) Title:</b> PROCESS FOR THE PRODUCTION OF GAMMA-BUTYROLACTONE  <b>(57) Abstract</b>  A new process for the production of gamma-Butyrolactone is described. Starting from maleic and/or succinic anhydride the conversion takes place in the presence of a catalyst composed of copper oxide and zinc oxide.		

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## Process for the Production of gamma-Butyrolactone

The present invention relates to a process for selective hydrogenation of maleic or succinic anhydride to gamma-butyrolactone (GBL) in the vapour phase using  
5 a catalyst comprising a mixed oxide of copper and zinc

GBL represents an example of a small volume commodity of great industrial interest, because of its increasing demand.

The main use of GBL is as intermediate for the synthesis of solvents with lower  
10 environmental impact than chlorinated ones, like pyrrolidone and N-methylpyrrolidone. It is also the raw material for the production of N-vinylpyrrolidone, of herbicides, pharmaceuticals and rubber additives.

The first works on GBL synthesis appeared in the 1940's, due to the start up of the Reppe process from acetylene and formaldehyde to give 1,4 butanediol  
15 (BDO) and then GBL by dehydrogenation. The drawbacks of this process are connected with the fluctuating prices of the raw materials and, mainly, with the hazard and the environmental impact of the use of both acetylene and formaldehyde.

During the second half of this century, other technologies have been studied  
20 and the number of patents about GBL production processes alternative to the Reppe process constantly increased.

The availability of maleic anhydride on industrial scale led to the development of new technologies for producing GBL, tetrahydrofuran (THF) or BDO by hydrogenation of maleic anhydride or of maleic anhydride derivatives like  
25 maleic acid diesters or succinic anhydride.

The liquid phase hydrogenation of maleic anhydride to GBL has been employed in commercial production, but never reached great industrial importance.

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Many patents describe the vapour phase hydrogenation of maleic anhydride or its esters, but mainly for the production of BDO; for instance WO 86/03189 describe the vapour phase hydrogenation of diethyl maleate to BDO.

WO 86/07358 describes a similar process for GBL production.

- 5 From a technological and economical point of view the esters of maleic acid or other maleic acid and/or succinic acid derivatives are less desirable raw materials compared with maleic anhydride.

Many patents describe the direct vapour phase hydrogenation of maleic anhydride to GBL, but none of the processes disclosed are completely  
10 satisfactory.

Some of these patents claim the use of copper chromites as catalysts (e.g. US Patent 3 065 243) but with unsatisfactory conversion and selectivity. Similar systems were claimed in US Patent 3 580 930 or in EP 332 140 (Cu/Zn/Cr/Al), but none of them are completely satisfactory in terms of GBL yield, productivity,  
15 by-products formation and catalyst durability.

Moreover chromium containing catalysts should not be the choice because of the negative environment impact of chromium, due to the toxicity of its compounds.

The WO 91/16132 disclose a process for the GBL production from maleic  
20 anhydride using a Cu/Zn/Al catalyst calcined at 400 - 525 °C. Such a high temperature is a draw-back in terms of plant design and operation.

Different catalytic systems, based on noble metal catalysts such as Cu/Pd and Cu/Pt have been described in e.g. US Patent 4 105 674. The cost of the noble metal is the draw back of these catalysts.

- 25 The object of the present invention is to provide a new and environmentally friendly process for the production of GBL by vapour phase hydrogenation of maleic anhydride and / or succinic anhydride with essentially quantitative conversion of the starting material, very high selectivity and using a commercial chromium-free catalyst.

The present invention provides a process for the vapour phase hydrogenation of maleic and / or succinic anhydride to GBL over a catalyst comprising a mixed oxide of copper and zinc.

The content of Copper as CuO is 50 - 90 wt% and Zinc as ZnO is 10 - 50 wt%.

5 Preferably the mixed oxide contains 60 - 80 wt% CuO and 20 - 40 % wt ZnO.

The catalyst composition may further contain inert components, such as tableting aids or inert fillers.

Preferred catalysts are commercially available e.g. from Süd Chemie, Germany.

10 In the active state, the catalytically active oxide material may include some metallic components (like metallic copper) formed in the activation step or during the hydrogenation.

The mixed oxide catalyst is commonly subjected to an activation treatment comprising gradually increasing its temperature from room temperature to 200 - 380 °C, preferably from room temperature to 250 - 300 °C in the presence  
15 of a hydrogen-containing gas.

The hydrogen-containing gas in the activation treatment may be a mixture of hydrogen and nitrogen. After the activation treatment the catalyst is ready for use. Activation requires a time usually varying from about 8 to 48 h, depending on reactor size and design.

20 The activation of the catalyst is exothermic. In case the reactor does not provide an efficient heat removal the hydrogen-containing gas must be suitably diluted or the space velocity must be increased to control exothermic peaks. Hydrogen dilution results in longer time for the exothermic phase of activation. Large adiabatic reactors usually requires the longest activation times.

25 During operation molten maleic anhydride or succinic anhydride or a mixture thereof is expediently vaporised in an hot hydrogen stream in a mixing section; the mixture can then be fed into the reactor packed with the above described activated catalyst. Optionally the catalyst can be packed between two layers of an essentially inert support material, possibly with the same size and shape of  
30 the catalyst. Suitable examples of essentially inert support materials include

silica, alumina, silica-alumina compound (e.g. mullite), silicon carbide, steatite and titania.

The reaction pressure is preferably between about 1 and 100 bar, more preferably between about 1 and 30 bar.

- 5 The molar ratio of hydrogen to the anhydride in the feed is between 10:1 and 300:1 and more preferably between 40:1 and 200:1. Lower hydrogen to anhydride ratios usually result in tar formation and short catalyst life, higher ratios tend to penalise the productivity of the catalyst.

- The reaction temperature is preferably between about 150 and 350 °C, and  
10 more preferably between 200 and 300 °C.

As it is well known by those skilled in the art, temperature and pressure range in the hydrogenation reaction depend on the desired product mixture.

Increasing temperature will result in the mix containing more THF, while increasing pressure will yield substantial amounts of BDO.

15

The following examples illustrate this invention in more detail.

**Example 1: (laboratory scale reactor)**

350 g of a commercial Cu/Zn catalyst, T-4322 from Süd Chemie AG (64 % CuO, 23.5 % ZnO), were packed in a 1 inch (2.54 cm) internal diameter tubular  
5 reactor; the resulting height of the bed was 0.7m.

The reactor was provided with an external jacket electrically heated to assure isothermicity all over the reactor length and with an axial thermowell with a movable thermocouple which was used to control and regulate the temperature in the catalyst bed.

- 10 The catalyst was activated in situ according to the following procedure:  
The temperature of the reactor was adjusted to 150 °C by means of the external jacket; a mixture of H<sub>2</sub>/N<sub>2</sub> was passed over the catalyst. To avoid hot spots the activation was performed gradually: the hydrogen content was gradually increased from 0 up to 8 % vol and the temperature was risen to 250  
15 °C. During the procedure the bed temperature was checked by means of the axial thermocouple. The increase of temperature and hydrogen content was controlled in order not to exceed  
20 20 - 25 °C as hot spot all along the catalytic bed. After reaching 250 °C the hydrogen content in the gas stream was gradually increased up to 100%. After  
5 hours at 250 °C in hydrogen, the activation was stopped.  
After catalyst activation a mixture of hydrogen and maleic anhydride was fed to the catalyst bed at ambient pressure. Hydrogenation conditions and performances are summarised in table 1.  
The maleic anhydride (MA) conversion was complete all over the tests. The  
25 yield of GBL was constantly over 95 % molar after the first 48 hours.

Table 1

T.O.S. (h)	MA feed (g/h)	H <sub>2</sub> /MA (molar ratio)	T (°C)	Molar Yields (%)			
				GBL	SA	THF	Others
48	14	141	228	95,6	0,5	0,4	3,5
140	11	175	229	95,3	0,0	0,6	4,1
150	12	165	228	97,7	0,0	0,3	2,3
177	18	109	237	97,6	0,1	0,2	2,1
209	8	236	233	96,2	0,0	0,5	3,3
272	12	158	259	95,1	0,7	0,1	4,1
GBL = $\gamma$ -butyrolactone; SA = succinic anhydride; THF = tetrahydrofuran; Others = mainly C <sub>2</sub> -C <sub>4</sub> alcohols and acids.							

T.O.S. = Time on Stream

5

### Example 2: (pilot reactor)

A tubular reactor with an internal diameter of 1 inch (2.54 cm) was packed with 1700 g of the same catalyst described in example 1; the resulting height of the bed was 3 m.

The reactor was provided with an external jacket with a circulation of diathermic oil and was equipped with an axial thermowell and a multipoint thermocouple. The catalyst was in-situ activated following the same procedure described in example 1.

After catalyst activation a mixture of hydrogen and maleic anhydride was fed to the catalyst bed at a pressure of 5 bar. Hydrogenation conditions and performances are summarised in table 2.

The MA conversion was complete all over the tests. The yield of GBL was always over 92 % molar and after the first 300 hours has constantly been over 95 % molar.

20



**Table 2**

T.O.S. (h)	MA feed (g/h)	H <sub>2</sub> /MA (molar ratio)	T (°C)	Molar Yields (%)			
				GBL	SA	THF	Others
28	118	136	234	92,6	1,2	4,0	2,2
158	126	126	235	93,0	2,0	3,0	1,8
272	137	102	239	94,1	0,5	3,2	2,1
372	157	102	245	96,5	0,1	1,3	2,2
539	170	94	248	95,5	0,1	2,3	1,7
645	208	70	270	94,9	0,6	1,8	3,3
692	219	67	270	95,5	0,3	1,3	3,0
765	222	61	264	96,6	0,4	1,0	1,8

GBL =  $\gamma$ -butyrolactone; SA = succinic anhydride;THF = tetrahydrofuran; Others = mainly C<sub>2</sub>-C<sub>4</sub> alcohols and acids.

T.O.S. = Time on Stream

**Claims:**

1. A process for the production of gamma-butyrolactone comprising  
catalytically hydrogenating maleic anhydride and / or succinic anhydride in a  
5      vaporous mixture with a hydrogen containing gas in contact with a catalyst  
comprising a catalytically active oxide material and optionally an inert  
support, wherein the catalytically active oxide material comprises a mixed  
oxide of copper and zinc, said mixed oxides being composed of 50 to 90  
wt% copper oxide and 10 to 50 wt% zinc oxide.  
10
2. A process according to claim 1 wherein said mixed oxides are composed of  
60 to 80 wt% copper oxide and 20 to 40 wt% zinc oxide.
3. A process according to claim 1 or 2 wherein the molar ratio of hydrogen to  
15      anhydride in the vaporous mixture of the hydrogen containing gas and the  
maleic anhydride and / or succinic anhydride is between 10 to 1 and 300 to  
1.
4. A process according to any one of claims 1 to 3 wherein the hydrogenation  
20      is conducted at a temperature of about 150 °C and 350 °C.
5. A process according to any one of claims 1 to 4 wherein the hydrogenation  
is conducted at a pressure of about 1 to 100 bar.

# INTERNATIONAL SEARCH REPORT

International Application No

PCT/EP 99/00003

**A. CLASSIFICATION OF SUBJECT MATTER**  
IPC 6 C07D315/00

According to International Patent Classification (IPC) or to both national classification and IPC

## B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 6 C07D

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	CHEMICAL ABSTRACTS, vol. 70, no. 23, 1969 Columbus, Ohio, US; abstract no. 77355x, page 283; XP002103357 see abstract & JP 06 814463 A (JAPAN GAS-CHEMICAL) 19 May 1968  --- -/--	1-5

☒ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

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## C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	CHEMICAL ABSTRACTS, vol. 119, no. 27, 1993 Columbus, Ohio, US; abstract no. 225800m, page 997; XP002103358 see abstract & PL 157 851 A (INSTYTUT CHEMII PRZEMYSLOWEJ) 31 July 1992 ---	1-5
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Information on patent family members

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